

What is claimed is:

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1. In an improved photohardenable composition composed of a cationically polymerizable and free radical polymerizable organic substance, a photo-generated acid precursor, a sensitizer for the photo-generated acid precursor and a free radical polymerization initiator wherein the improvement comprises:

a) a mixture of photopolymerizable resins consisting essentially of at least two epoxy resins one of which polymerizes at a slower rate and has a higher neat viscosity than at least one other epoxy resin present and [the epoxy resins are] said one of which epoxy resin is present at a concentration in the mixture of from 5 to 25% by weight, and at least one monoacrylic monomer and at least one multi-acrylic monomer wherein the concentration of the monoacrylic monomer is from 0.12 to 0.90 parts by weight that of the multiacrylic monomer and wherein the ratio of the weight of the epoxy resins to that of the acrylic monomers is between 3 to 10; and

b) a combination of a free radical initiator and a photo-generating acid precursor characterized by optical molar extinction coefficients and optimized for use with a multi-wavelength argon ion laser operating in the UV and producing two major wavelengths of 351 nm and 364 nm such that a normalized ratio of the extinction coefficients of the precursor and the initiator at one major wavelength is less than 3 times the ratio of extinction coefficient at a second major wavelength.

2. A method for accurately fabricating an integral three dimensional article having improved green strength by controlling the diffusion of photoactivated molecular species in the regions of a photohardenable liquid composition exposed to actinic radiation, the method comprising the steps of:

(a) forming a layer of the photohardenable liquid composition;

(b) imagewise exposing areas of at least a portion of the layers to actinic radiation at wavelengths of 351 nm and 364 nm;

(c) introducing a new layer of liquid on to the layer previously exposed imagewise in step (b);

(d) imagewise exposing at least a portion of the new liquid layer to actinic radiation, wherein the improvement comprises use of photohardenable liquid composition comprising:

a) a mixture of photopolymerizable resins consisting essentially of at least two epoxy resins one of which polymerizes at a slower rate and has a higher neat viscosity than at least one other epoxy resin present and [the epoxy resins are] said one of which epoxy resin is present at a concentration in the mixture of from 5 to 25% by weight, and at least one monoacrylic monomer and at least one multi acrylic monomer wherein the concentration of the monoacrylate monomer is from 0.12 to 0.90 parts by weight that of the multi-acrylate monomer and wherein the ratio of the weight of the epoxy resins to that of the acrylic monomers is between 3 to 10; and

b) a combination of a free radical initiator and a photo-generating acid precursor characterized by optical molar extinction coefficients and optimized for use with a multi-wavelength argon ion laser operating in the UV and producing two major wavelengths of 351 nm and 364 nm such that a normalized ratio of the extinction coefficients of the precursor and the initiator at one major wavelength is less than 3 times the ratio of extinction coefficient at a second major wavelength.

3. A composition comprising:

a mixture of cationically polymerizable components having,

a) at least one low-viscosity, fast-curing cationically polymerizable component, and

b) at least one high-viscosity, slow-curing cationically polymerizable component; and

at least one radically polymerizable component.

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4. The composition of claim 3 wherein said composition further comprises at least one photo-generating acid precursor and at least one free radical initiator.
 5. The composition of claim 3 wherein said high-viscosity, slow-curing cationically polymerizable component has a viscosity of greater than 1000 poise @ 25°C.
 6. The composition of claim 3 wherein said high-viscosity, slow-curing cationically polymerizable component has a viscosity of greater than 200 poise @ 52°C.
 7. The composition of claim 5 wherein said high-viscosity, slow-curing cationically polymerizable component has a softening point below 40°C.
 8. The composition of claim 3 wherein said mixture of cationically polymerizable components comprises from 5 to 25% by weight of said high-viscosity, slow-curing cationically polymerizable component.
 9. The composition of claim 8 wherein said high-viscosity, slow-curing cationically polymerizable component has a viscosity of greater than 1000 poise @ 25°C.
 10. The composition of claim 3 wherein said at least one radically polymerizable component includes at least one mono-functional acrylate monomer.
 11. The composition of claim 10 wherein said at least one radically polymerizable component further includes at least one multi-functional acrylate monomer.
 12. The composition of claim 11 wherein the total amount of mono-functional acrylate monomers to the total amount of multi-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.12 to 0.9.
 13. The composition of claim 11 wherein the total amount of mono-functional acrylate monomers to the total amount of multi-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.27 to 0.58.

14. The composition of claim 10 wherein said at least one radically polymerizable component further includes at least one tri-functional acrylate monomer.
15. The composition of claim 14 wherein the total amount of mono-functional acrylate monomers to the total amount of tri-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.12 to 0.9.
16. The composition of claim 14 wherein the total amount of mono-functional acrylate monomers to the total amount of tri-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.27 to 0.58.
17. The composition of claim 3 wherein said at least one radically polymerizable component further includes a blend of radically polymerizable monomers comprising said at least one mono-functional acrylate monomer and at least one multi-functional acrylate monomer.
18. The composition of claim 17 wherein the ratio, on a weight basis, of said blend of radically polymerizable monomers to said mixture of cationically polymerizable components is from 3 to 10.
19. The composition of claim 3 wherein said high viscosity, slow-curing cationically polymerizable component includes an epoxy phenolic novolac resin and/or an epoxy cresol novolac resin.
20. The composition of claim 19 wherein said epoxy phenolic novolac resin has a functionality of 3.6 or more.
21. The composition of claim 3 wherein said low-viscosity, fast-curing cationically polymerizable component includes at least one cycloaliphatic epoxy.
22. The composition of claim 4 wherein said composition further comprises a sensitizer for the photo-generated acid precursor.

23. The composition of claim 3 wherein said at least one radically polymerizable component includes tetrahydrofurfuryl acrylate, isobornyl acrylate, lauryl acrylate and/or caprolactone acrylate.
24. The composition of claim 3 wherein said at least one radically polymerizable component includes a radically polymerizable compound having hydroxyl functionality.
25. The composition of claim 3 wherein said at least one radically polymerizable component includes caprolactone acrylate.
26. A photohardenable composition comprising:
a mixture of cationically polymerizable resins consisting essentially of at least two epoxy resins wherein a first epoxy resin polymerizes at a slower rate and has a higher neat viscosity than a second epoxy resin,
at least one mono-functional acrylate monomer,
a photo-generated acid precursor, and
a free radical polymerization initiator.
27. The photohardenable composition of claim 26 wherein said composition further comprises a multi-functional acrylate monomer.
28. The photohardenable composition of claim 27 wherein the total amount of mono-functional acrylate monomers to the total multi-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.12 to 0.9.
29. The photohardenable composition of claim 27 wherein the total amount of mono-functional acrylate monomers to the total amount of multi-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.27 to 0.58.

30. The photohardenable composition of claim 27 wherein the ratio, on a weight basis, of said mixture of cationically polymerizable resins to said mono-functional acrylate and multi-functional acrylate monomers is from 3 to 10.
31. The photohardenable composition of claim 26 wherein said first epoxy resin comprises an epoxy phenolic novolac resin and/or an epoxy cresol novolac resin.
32. The photohardenable composition of claim 31 wherein said epoxy phenolic novolac resin has a functionality of 3.6 or more.
33. The photohardenable composition of claim 26 wherein said second epoxy resin comprises at least one cycloaliphatic epoxy.
34. The photohardenable composition of claim 26 wherein said composition further comprises a tri-functional acrylate monomer.
35. The photohardenable composition of claim 26 wherein said at least one mono-functional acrylate monomer includes tetrahydrofurfuryl acrylate, isobornyl acrylate, lauryl acrylate and/or caprolactone acrylate.
36. The photohardenable composition of claim 26 wherein said at least one mono-functional acrylate monomer includes a radically polymerizable compound having hydroxyl functionality.
37. The photohardenable composition of claim 26 wherein said at least one mono-functional acrylate monomer includes caprolactone acrylate.
38. The photohardenable composition of claim 26 wherein said composition further comprises a sensitizer for the photo-generated acid precursor.
39. A method for fabricating a three-dimensional article comprising:
- a. forming a layer of a composition comprising,
a mixture of cationically polymerizable components having,

i) at least one low-viscosity, fast-curing cationically polymerizable component, and

ii) at least one high-viscosity, slow-curing cationically polymerizable component, and

at least one radically polymerizable component;

b. imagewise exposing areas of at least a portion of the layer to actinic radiation; and

c. introducing a new layer of said composition on to the layer previously exposed imagewise in step (b) and repeating step (b).

40. The method of claim 39 wherein said composition further comprises at least one photo-generating acid precursor and at least one free radical initiator.

41. The method of claim 39 wherein said high-viscosity, slow-curing cationically polymerizable component has a viscosity of greater than 1000 poise @ 25°C.

42. The method of claim 39 wherein said high-viscosity, slow-curing cationically polymerizable component has a viscosity of greater than 200 poise @ 52°C.

43. The method of claim 41 wherein said high-viscosity, slow-curing cationically polymerizable component has a softening point below 40°C.

44. The method of claim 39 wherein said mixture of cationically polymerizable components comprises from 5 to 25% by weight of said high-viscosity, slow-curing cationically polymerizable component.

45. The method of claim 44 wherein said high-viscosity, slow-curing cationically polymerizable component has a viscosity of greater than 1000 poise @ 25°C.

46. The method of claim 39 wherein said at least one radically polymerizable component includes at least one mono-functional acrylate monomer.

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47. The method of claim 46 wherein said at least one radically polymerizable component further includes at least one multi-functional acrylate monomer.
48. The method of claim 47 wherein the total amount of mono-functional acrylate monomers to the total amount of multi-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.12 to 0.9.
49. The method of claim 47 wherein the total amount of mono-functional acrylate monomers to the total amount of multi-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.27 to 0.58.
50. The method of claim 46 wherein said at least one radically polymerizable component further includes at least one tri-functional acrylate monomer.
51. The method of claim 50 wherein the total amount of mono-functional acrylate monomers to the total amount of tri-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.12 to 0.9.
52. The method of claim 50 wherein the total amount of mono-functional acrylate monomers to the total amount of tri-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.27 to 0.58.
53. The method of claim 39 wherein said at least one radically polymerizable component further includes a blend of radically polymerizable monomers comprising said at least one mono-functional acrylate monomer and at least one multi-functional acrylate monomer.
54. The method of claim 53 wherein the ratio, on a weight basis, of said blend of radically polymerizable monomers to said mixture of cationically polymerizable components is from 3 to 10.

55. The method of claim 39 wherein said high viscosity, slow-curing cationically polymerizable component includes an epoxy phenolic novolac resin and/or an epoxy cresol novolac resin.
56. The method of claim 55 wherein said epoxy phenolic novolac resin has a functionality of 3.6 or more.
57. The method of claim 39 wherein said low-viscosity, fast-curing cationically polymerizable component includes at least one cycloaliphatic epoxy.
58. The method of claim 55 wherein said low-viscosity, fast-curing cationically polymerizable component includes at least one cycloaliphatic epoxy.
59. The method of claim 40 wherein said composition further comprises a sensitizer for the photo-generated acid precursor.
60. A method of forming a photohardenable composition comprising:
- a. forming a mixture of epoxy resins having a first epoxy resin which polymerizes at a slower rate and has a higher neat viscosity than a second epoxy resin, and
 - b. mixing in a free radical polymerizable substance.
61. The method of claim 60 further comprising adding a photo-generated acid precursor, and a free radical polymerization initiator.
62. The method of claim 61 further comprising admixing a sensitizer for the photo-generated acid precursor.
63. The method of claim 60 wherein said free radical polymerizable substance includes a multi-functional acrylate monomer.
64. The method of claim 60 wherein said free radical polymerizable substance includes a tri-functional acrylate monomer.

65. The method of claim 60 wherein said free radical polymerizable substance includes a mono-functional acrylate monomer.
66. The method of claim 65 wherein said free radical polymerizable substance further includes a multi-functional acrylate monomer.
67. The method of claim 65 wherein said free radical polymerizable substance further includes a tri-functional acrylate monomer.
68. The method of claim 66 wherein the total amount of mono-functional acrylate monomers to the total amount of multi-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.12 to 0.9.
69. The method of claim 66 wherein the total amount of mono-functional acrylate monomers to the total amount of multi-functional acrylate monomers present in the composition, on a parts by weight basis relative to the total composition, is 0.27 to 0.58.
70. The method of claim 60 wherein said free radical polymerizable substance comprises a blend of at least one mono-functional acrylate monomer and at least one multi-functional acrylate monomer.
71. The method of claim 70 wherein the ratio, on a weight basis, of said mixture of epoxy resins to said free radical polymerizable substance is from 3 to 10.
72. The method of claim 60 wherein said first epoxy resin comprises an epoxy phenolic novolac resin and/or an epoxy cresol novolac resin.
73. The method of claim 72 wherein said epoxy phenolic novolac resin has a functionality of 3.6 or more.
74. The method of claim 60 wherein said second epoxy resin comprises at least one cycloaliphatic epoxy.

75. The method of claim 60 wherein said first epoxy resin has a viscosity of greater than 1000 poise @ 25°C.
76. The method of claim 60 wherein said first epoxy resin has a viscosity of greater than 200 poise @ 52°C.
77. The method of claim 76 wherein said first epoxy resin has a softening point below 40°C.
78. The method of claim 60 wherein said mixture of epoxy resins comprises from 5 to 25% by weight of said first epoxy resin.
79. The method of claim 75 wherein said mixture of epoxy resins comprises from 5 to 25% by weight of said first epoxy resin.
80. A composition comprising:
- a mixture of epoxy resins comprising from 5 to 25% by weight, relative to the total mixture, of at least one high-viscosity, slow-curing epoxy, wherein said high-viscosity, slow-curing cationically polymerizable component has a viscosity of greater than 1000 poise @ 25°C and a softening point below 40°C, and at least one low-viscosity, fast-curing epoxy,
 - a blend of acrylate functional monomers comprising at least one multi-functional acrylate monomer and at least one mono-functional acrylate, wherein the ratio of said at least one mono-functional acrylate monomer to said at least one multi-functional acrylate monomer, on a parts by weight basis relative to the total composition, is 0.12 to 0.9,
 - at least one photo-generating acid precursor, and
 - at least one free radical initiator,
 - wherein the ratio, on a weight basis, of said blend of epoxy resins and said blend of functional acrylate monomers is from 3 to 10.

81. A method of forming a three-dimensional article comprising:
processing the composition of claim 80 to form a solid image.
82. A method of forming the composition of claim 80 comprising:
forming said composition by combining said mixture of epoxy resins, said
blend of acrylate functional monomers, said at least one photo-generating acid
precursor, and said at least one free radical initiator.
83. An article formed from the composition of claim 80.